

# Chapter 0: Quantum Mechanics

## 1 Schrödinger Equation

In classical mechanics, we talk about a particle say an electron with a position  $x$  and velocity  $v$ . In quantum mechanics, particle state is represented by complex waves  $\exp(ikx)$  or sum of such waves  $\sum_j \exp(ik_j x)$ . In complex wave  $\exp(ikx)$ ,  $k$  is the wavenumber of the particle. The wave evolves in time as  $\exp(i(kx - \omega(k)t))$ ,  $\omega(k)$  is the frequency of the wave and depends on wavenumber  $k$ . The dependence  $\omega(k)$  is called the dispersion relation of the wave. First postulate of quantum mechanics is that the energy of the wave is  $E = \hbar\omega(k)$ , where  $\hbar$  is a fundamental constant called Planck's constant. Its units are angular momentum and in SI units its value is  $6.6 \times 10^{-34}$ .

Consider a classical particle of mass  $m$  moving with velocity  $v$  in frame  $O'$ . Its kinetic energy is  $\frac{1}{2}mv^2$ . If no work is done on the system with a force then this energy is conserved. Furthermore this is conserved in all frames of reference. The kinetic energy in frame  $O$  in which the frame  $O'$  moves with velocity  $u$  is  $E(u) = \frac{1}{2}m(v + u)^2$ . For infinitesimal  $u$ ,  $E(u) \sim \frac{1}{2}mv^2 + mvu$  and since energy is conserved in this new frame  $mv = \frac{dE}{du}$  is conserved. This quantity  $\frac{dE}{du}$  is called momentum. Using this interpretation of momentum, we can calculate the momentum of the complex wave. For this, we develop a little bit of theory of relativity.

### 1.1 Relativity

Consider lab frame  $O$  and a frame  $O'$ , moving with respect to lab frame with velocity  $v$ .

Then the space time increment  $(\Delta x, \Delta t)$  in  $O$ , corresponds to  $(\Delta x', \Delta t')$  in  $O'$ . The phase increment of the light wave in both frames is the same.

Then

$$k\Delta x - \omega\Delta t = k'\Delta x' - \omega'\Delta t' \quad (1)$$

$$k(\Delta x - c\Delta t) = k'(\Delta x' - c\Delta t'). \quad (2)$$

For light travelling in opposite direction

$$k'(\Delta x + c\Delta t) = k(\Delta x' + c\Delta t'). \quad (3)$$

The two relations give

$$(c\Delta t)^2 - \Delta x^2 = (c\Delta t')^2 - \Delta x'^2. \quad (4)$$

For  $\Delta x' = 0$ , we have,  $\Delta x = v\Delta t$  and this gives

$$\Delta t = \frac{\Delta t'}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (5)$$

This is called time dilation. Furthermore

$$\frac{k'}{k} = \frac{1 - \frac{v}{c}}{\sqrt{1 - \frac{v^2}{c^2}}} \quad (6)$$

Then combining Eq. (2, 3, 6), we get

$$\begin{bmatrix} \Delta x \\ c\Delta t \end{bmatrix} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} \quad (7)$$

For a rod of length  $l'$  in  $O'$  we have  $(\Delta x', \Delta t') = (l', 0)$ , the  $l = \Delta x - v\Delta t = l' \sqrt{1 - \frac{v^2}{c^2}}$ . This is called length contraction.

For an object moving at velocity in the frame  $O'$  at velocity  $u$ , for time  $\Delta t'$ , we have  $(\Delta x', \Delta t') = (u\Delta t', \Delta t')$ . Then from (Eq. 7), the relative velocity

$$v = \frac{\Delta x}{\Delta t} = \frac{u + v}{1 + \frac{uv}{c^2}} \quad (8)$$

Consider a electron matter wave with frequency, wavevector  $(\omega, k)$  and  $(\omega', k')$  respectively. Then

The phase increment of the matter wave in both frames is the same.

Then

$$k\Delta x - \omega\Delta t = k'\Delta x' - \omega'\Delta t' \quad (9)$$

$$\begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \begin{bmatrix} \Delta x \\ c\Delta t \end{bmatrix} = \begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} = \begin{bmatrix} k' & -\frac{\omega'}{c} \end{bmatrix} \begin{bmatrix} \Delta x' \\ c\Delta t' \end{bmatrix} \quad (10)$$

This gives

$$\begin{bmatrix} k & -\frac{\omega}{c} \end{bmatrix} \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} = \begin{bmatrix} k' & -\frac{\omega'}{c} \end{bmatrix} \quad (11)$$

Rewriting this equation we get

$$\begin{bmatrix} k \\ \frac{\omega}{c} \end{bmatrix} = \frac{1}{\sqrt{1 - \frac{v^2}{c^2}}} \begin{bmatrix} 1 & \frac{v}{c} \\ \frac{v}{c} & 1 \end{bmatrix} \begin{bmatrix} k' \\ \frac{\omega'}{c} \end{bmatrix} \quad (12)$$

Then the energy

$$E(v) = \hbar\omega(v) = \frac{\hbar}{\sqrt{1 - \frac{v^2}{c^2}}} (vk' + \omega'). \quad (13)$$

Once again we use our interpretation of momentum and ask what is  $\frac{dE(v)}{dv}|_0 = \hbar k'$ . Therefore momentum of our complex wave  $\omega', k'$  is simply

$$\hbar k'.$$

Thus we have two basic results in quantum mechanics the energy is  $\hbar\omega$  and momentum  $\hbar k$ .

Now from classical mechanics  $E = \frac{p^2}{2m}$ . Then we get  $\hbar\omega = \frac{\hbar^2 k^2}{2m}$  or  $\omega = \frac{\hbar k^2}{2m}$ . Thus my complex wave  $\psi(x, t) = \exp(i(kx - \omega t))$  satisfies

$$i\hbar \frac{\partial \psi}{\partial t} = \left(-\frac{\hbar^2}{2m} \frac{\partial^2 \psi}{\partial x^2}\right). \quad (14)$$

This equation (14) is called *Schrödinger* equation. It is still true if we have

$$\psi(x, t) = \sum_j \alpha_j \exp(i(k_j x - \omega(k_j)t)).$$

as individual exponential satisfy these equation.

$\psi(x, t)$  is called a wavefunction of electron, it is superposition of plane waves. This is a feature of quantum mechanics, we can be in superposition of states. It satisfies the Schrödinger equation. All we are saying is that if we start with initial state  $\psi(x) = \sum_j \alpha_j \exp(ik_j x)$ , these ways will evolve by their characteristic energies as  $\psi(x, t) = \sum_j \alpha_j \exp(i(k_j x - \omega(k_j)t))$  and  $\psi(x, t)$  satisfies the Schrödinger equation.

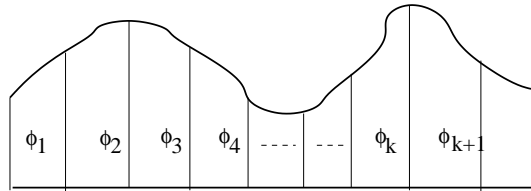


Figure 1: Figure shows how  $V(x)$  is decomposed as piecewise constant potential.

Now how does my wavefunction evolve if I have a potential  $V$ . Then from classical mechanics  $E - V = \frac{p^2}{2m}$ , implying  $\hbar\omega - V = \frac{\hbar^2 k^2}{2m}$  or my wave satisfies

$$i\hbar \frac{\partial \psi}{\partial t} = \left(-\hbar \frac{\partial^2}{\partial x^2} + V\right)\psi. \quad (15)$$

and again same is true if we have superposition of plane waves.

Now how does the evolution of  $\psi(x)$  take place when we have  $V(x)$ . Then we can break  $\psi(x)$  into small pieces  $\phi_i$  over which  $V(x)$  is constant as  $V_i$ . See fig 1. Then each  $\phi_i$  sees a potential  $V_i$ . Its evolution will be same if  $V_i$  was globally true. Then we can break  $\phi$  into exponentials and conclude it satisfies the equation

$$i\hbar \frac{\partial \phi_i}{\partial t} = \left(-\hbar \frac{\partial^2}{\partial x^2} + V_i\right)\phi_i. \quad (16)$$

Then adding them all we get

$$i\hbar \frac{\partial \psi}{\partial t} = \left(-\hbar \frac{\partial^2}{\partial x^2} + V(x)\right)\psi. \quad (17)$$

Thus we have derived a fundamental equation of quantum mechanics. Wavefunction  $\psi(x)$  has a probabilistic interpretation.  $\int_a^b |\psi(x)|^2 dx$  gives the probability of finding the particles in the interval  $[a, b]$

Lets take sum of such complex waves with  $k_j$  centered around  $k_0$ . Then using  $\Delta k_j = k_j - k_0$ , with  $\Delta k_j \in [-B, B]$ , such that  $\Delta k$  is the spacing between successive  $\Delta k_j$ , we have

$$\phi(x) = \sum_j \exp(ik_j x) = \exp(ik_0 x) \sum_j \exp(i\Delta k_j x) = 2 \exp(ik_0 x) \sum_j \cos(\Delta k_j x) \quad (18)$$

$$= 2 \exp(ik_0 x) \frac{\sin(Bx)}{\Delta k x} = 2 \exp(ik_0 x) \frac{B}{\Delta k} \frac{\sin(Bx)}{Bx}. \quad (19)$$

We summarize,

## 2 Wave Mechanics

lets Recap. The free electron wavefunction is  $\psi = \exp(ikx)$ . The momentum is  $\frac{\hbar}{i} \frac{\partial}{\partial x}$ . This gives the kinetic energy  $\epsilon = \frac{p^2}{2m} = \frac{\hbar^2 k^2}{2m}$ , which for  $\epsilon = \hbar\omega$  gives,

$$\omega(k) = \frac{\hbar k^2}{2m}. \quad (20)$$

The dispersion is a parabola as shown below in figure 2 A.

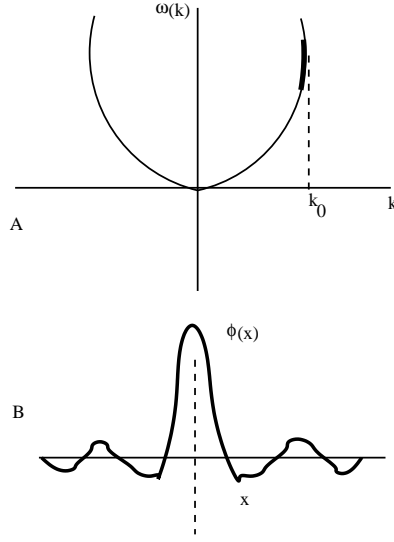


Figure 2: Figure A shows the dispersion  $\omega(k)$  vs  $k$  for a free electron. Figure B shows a wavepacket centered at  $k_0$ .

Now, consider a wavepacket centered at  $k_0$  shown in figure 2 A, B. The packet takes the form

$$\phi(x) = \frac{1}{\sqrt{N}} \sum_j \exp(ik_j x), \quad \phi(x, t) = \frac{1}{\sqrt{N}} \sum_j \exp(-i\omega(k_j)t) \exp(ik_j x), \quad (21)$$

where  $\omega(k_j) = \omega(k_0) + \omega'(k_0)\Delta k_j$  where  $\Delta k_j = k_j - k_0$ . Denote  $v_g = \omega'(k_0) = \frac{\hbar k_0}{m}$ , as the group velocity. Then

$$\phi(x, t) = \frac{1}{\sqrt{N}} \exp(i(k_0 x - \omega(k_0)t)) \sum_j \exp(i\Delta k_j(x - v_g t)). \quad (22)$$

The function  $f(x) = \frac{1}{\sqrt{N}} \sum_j \exp(i\Delta k_j x) = \frac{2}{\sqrt{N}} \sum_j \cos(\Delta k_j x)$ , is centered at origin with width  $\propto (\Delta k)^{-1}$  as shown in figure 2 B. Then

$$|\phi(x, t)| = |f(x - v_g t)|, \quad (23)$$

the free electron wavepacket moves with a group velocity  $v_g$ .

Now let's apply an electrical field  $E$  in the  $x$  direction at  $t = 0$ . Then the Schrödinger equation is

$$i\hbar \frac{\partial \psi}{\partial t} = \frac{1}{2m} \left(-i\hbar \frac{\partial}{\partial x}\right)^2 \psi + eEx \psi. \quad (24)$$

The equation is satisfied by time varying wavevectors  $\exp(ik(t)x)$ , where  $k(t) = k - \frac{eEt}{\hbar}$ , with energy (dispersion)  $\omega(k(t)) = \frac{\hbar k(t)^2}{2m} = \frac{\hbar(k - \frac{eEt}{\hbar})^2}{2m}$ , so that the wavefunction becomes

$$\exp(-i \int_0^t \omega(k(\tau)) d\tau) \exp(ik(t)x).$$

The initial wavepacket  $\phi(x)$  evolves to  $\phi(x, t)$ , where,

$$\phi(x) = \frac{1}{\sqrt{N}} \sum_j \exp(ik_j x), \quad \phi(x, t) = \frac{1}{\sqrt{N}} \sum_j \exp(-i \int_0^t \omega(k_j(\tau)) d\tau) \exp(ik_j(t)x). \quad (25)$$

The group velocity

$$v_g(t) = \frac{\hbar k(t)}{m} = \frac{\hbar(k - \frac{eEt}{\hbar})}{m}; \quad \frac{dv_g(t)}{dt} = -\frac{eE}{m}. \quad (26)$$

The electron wavepacket simply accelerates the way we know from classical mechanics. Being more pedagogical, we have

$$\begin{aligned} \phi(x, t) &= \frac{1}{\sqrt{N}} \sum_j \exp(-i \int_0^t \omega(k_j(t)) ) \exp(ik_j(t)x) \\ &= \frac{1}{\sqrt{N}} \exp(-i \int_0^t \omega(k_0(t)) ) \exp(ik_0(t)x) \sum_j \exp(i\Delta k_j(x - \int_0^t v_g(\sigma) d\sigma)). \end{aligned} \quad (27)$$

The wavepacket evolves with instantaneous velocity  $v_g(t)$ .

The above method can be generalized to arbitrary potential. Consider the Schrödinger equation

$$i\hbar \frac{\partial \psi}{\partial t} = (-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} - eV(x))\psi. \quad (28)$$

We approximate the potential  $V$  by piecewise linear potential such that  $V(x) = V(x_i) + V'(x_i)\delta x$ , where  $\delta x = x - x_i$ , as shown in figure 3. We call these regions of linearized potential, cells. We can rewrite the potential in a cell as  $V(x) = U(x_i) + V'(x_i)x$

We assume that the wavepacket has large  $k_0$  such that  $\Delta k \sim \sqrt{k_0}$  is large and therefore for the wavepacket,  $\Delta x \sim (\Delta k)^{-1}$  is small so that it fits well within one cell. Then in this cell, the Schrödinger equation takes the form

$$i\hbar \frac{\partial \psi}{\partial t} = (-\frac{\hbar^2}{2m} \frac{\partial}{\partial x^2} - eV'(x_i)x - eU(x_i))\psi. \quad (29)$$

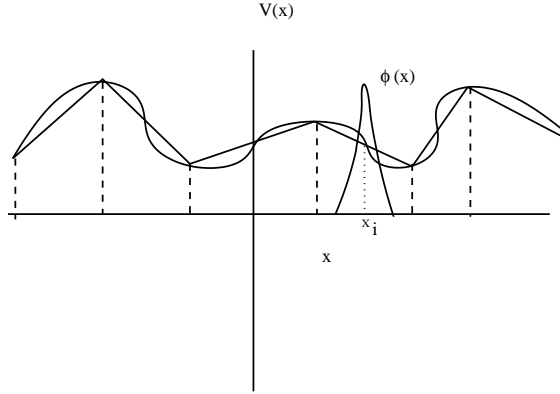


Figure 3: Figure shows linear approximation of potential  $V(x)$ . The wavepacket  $\phi(x)$  is confined to a cell.

Since the wavepacket is confined to a cell, its evolution would be the same if the potential were not only true in the cell but globally true. This is because the wavepacket doesn't know what the potential is outside the cell, it's confined to the cell. Then let's solve the Schrödinger equation with this potential assumed globally true and see how the wavepacket evolves.

Then as before for the Schrödinger equation is solved by wavevector  $\psi = \exp(ik(t)x)$ . Let  $x(t)$  denote the coordinates of the center of the wavepacket, then

$$k(t) = k + \frac{e \int_0^t V'(x(\tau)) d\tau}{\hbar}, \quad \omega(k(t)) = \frac{\hbar \left( k + \frac{e \int_0^t V'(x(\tau)) d\tau}{\hbar} \right)^2}{2m} - \frac{e \int_0^t U(x(\tau)) d\tau}{\hbar}. \quad (30)$$

The group velocity

$$v_g(t) = \frac{\hbar \left( k + \frac{e \int_0^t V'(x(\tau)) d\tau}{\hbar} \right)}{m}; \quad \frac{dv_g(t)}{dt} = \frac{e V'(x(t))}{m}. \quad (31)$$

This is classical mechanics. Therefore at high energies where  $k_0$  is large and the wavepacket is well confined, i.e., over the packet width, the second-order change of potential is small,  $V''(x)\Delta x \ll V'(x)$ . A linearized potential is a good approximation and evolution in quantum mechanics mimics classical mechanics.

### 3 Particle in a Square Well

In this section we solve the Schrödinger equation with a special potential. The Schrödinger equation has the form

$$i\hbar \frac{\partial \psi}{\partial t} = H\psi \quad (32)$$

$H(x)$  is the Hamiltonian of the system, it is an operator. If we can find eigenfunctions of  $H$  call  $\phi_i$  with energies  $E_i$ . Then the eigenfunction  $\phi_i$  evolves as  $\exp(-i\frac{E_i t}{\hbar})\phi_i(x)$ . Given initial wavefunction  $\psi(x) = \sum_i \alpha_i \phi_i(x)$ , we have  $\psi(x, t) = \sum_i \alpha_i \exp(-i\frac{E_i t}{\hbar})\phi_i(x)$ . Therefore all the challenge is in finding  $\phi_i(x)$ . These are called stationary states, eigenfunctions, etc.

Lets take a potential as show in figure 4 which is  $-V$  in region  $II$  and zero elsewhere.

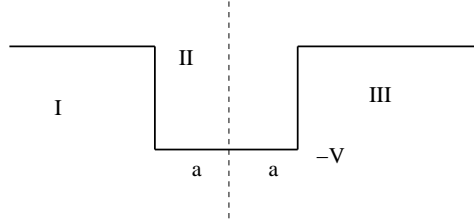


Figure 4: Figure shows a potential well of depth  $V$ .

We solve for

$$H\phi = E\phi.$$

We first do it in region  $II$  that gives

$$\left(-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} - V\right)\phi = E\phi \quad (33)$$

$$-\frac{\hbar^2}{2m} \frac{\partial^2}{\partial x^2} \phi = (E + V)\phi \quad (34)$$

then the solution is  $\exp(ikx)$  and  $\exp(-ikx)$  where  $k = \frac{\sqrt{2m(E+V)}}{\hbar}$ .

In region  $I$  we have solution is  $\phi_1 = \exp(k_1x)$ , where  $k_1 = \frac{\sqrt{-2mE}}{\hbar}$ .  $E$  should be negative as solution should die to 0 at  $-\infty$ . In region  $III$  we have solution is  $\phi_3 = \exp(-k_1x)$ , as solution should die to 0 at  $\infty$ . In region 2, we can say we have a solution  $\phi_2 = A \exp(ikx) + B \exp(-ikx)$  we match it to solution in  $I$  and  $III$ . Then we have

$$\frac{\phi_1'(-a)}{\phi_1(-a)} = \frac{\phi_2'(-a)}{\phi_2(-a)}, \quad \frac{\phi_3'(a)}{\phi_3(a)} = \frac{\phi_2'(a)}{\phi_2(a)}. \quad (35)$$

From this we get

$$\frac{\phi_2'(-a)}{\phi_2(-a)} = -\frac{\phi_2'(a)}{\phi_2(a)}. \quad (36)$$



which gives  $A = B$  from which we get for  $z_0 = \frac{\sqrt{2mV}}{\hbar}$ ,

$$k_1 = k \tan ka; \quad (37)$$

Let  $z = ka$  and  $z_0 = \frac{a\sqrt{2mV}}{\hbar}$ , with  $z < z_0$  from which we get

$$\underbrace{\tan z}_{f_1(z)} = \underbrace{\sqrt{(z_0/z)^2 - 1}}_{f_2(z)} \quad (38)$$

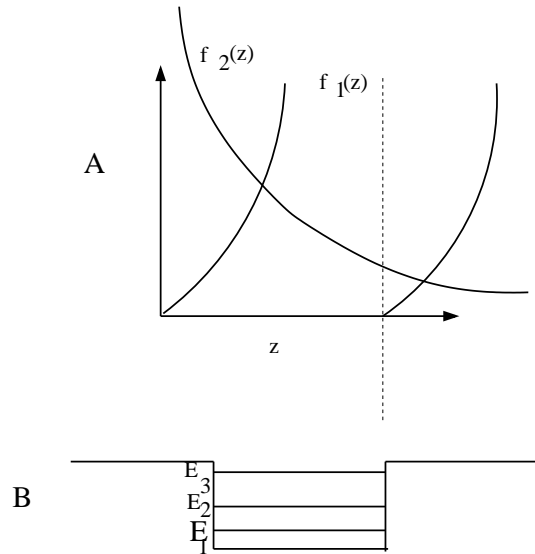


Figure 5: Figure A shows plots of  $f_1(z)$  and  $f_2(z)$ . The energies are depicted in fig B.

When  $n\pi < z < (n+1)\pi$ , we get  $n$  intersections as shown in fig 9A . These are bound solutions. The energies are depicted in fig 9B. Until now we talked about bound states. when total energy  $E < 0$ . They are like a ball stuck in pit and keeps going back and forth as in Fig. A in 6. There are other states as shown in Fig. A in 6 when  $E > 0$ , then ball rolls from left crosses the pit and moves to right. Lets find quantum mechanical analog of these scattering states.

Since  $E > 0$ , we have  $k_1 = \frac{\sqrt{2mE}}{\hbar}$ . Assume a incident wave (ball) from left  $\exp(ik_1x)$ , part of which is reflected  $R \exp(-ikx)$  and part transmitted on right hand side  $T \exp(ikx)$ . Then we have wavefunction  $\exp(ik_1x) + R \exp(-ik_1x)$  in region I and  $A \exp(ikx) + B \exp(-ikx)$

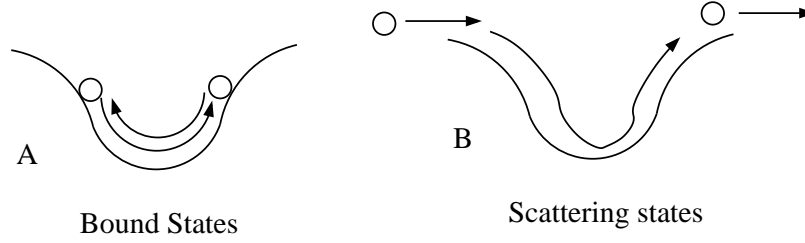


Figure 6: Figure A shows bound states. Figure B shows scattering states

in region  $II$  and  $T \exp(ikx)$  in region 3. We have 4 boundary conditions

$$\begin{aligned} \exp(-ik_1a) + R \exp(ik_1a) &= A \exp(-ika) + B \exp(ika). \\ T \exp(ik_1a) &= A \exp(ika) + B \exp(-ika). \\ k_1(\exp(-ik_1a) - R \exp(ik_1a)) &= k(A \exp(-ika) - B \exp(ika)). \\ k_1 T \exp(ik_1a) &= k(A \exp(ika) - B \exp(-ika)). \end{aligned}$$

On solving we get

$$\begin{aligned} T &= \frac{\exp(-i2k_1a)}{\cos(2ka) - i \frac{k^2 + k_1^2}{2kk_1} \sin(2ka)}. \\ R &= -i \frac{k^2 - k_1^2}{2kk_1} \sin(2ka) T. \end{aligned}$$

All energies  $E > 0$  are allowed as scattering states.

## 4 Infinite Square Well

Figure shows an infinite square well which has zero potential in the center and infinite potential  $V = \infty$  outside. Let the eigen energy of  $\phi$  be  $E_0$  then  $\langle E \rangle = E_0$ . But then  $\phi$  cannot have an presence outside center region else  $\langle E \rangle = \infty$ . Therefore  $\phi$  is confined to center region.  $\phi$  has to be continuous (else its double derivative is  $\infty^2$  which cannot satisfy the Schrödinger equation). Then we look for

$$-\frac{\partial^2 \phi}{\partial x^2} = E_0 \phi$$

which gives  $\phi_n = \cos(\frac{n\pi x}{2a})$  with energies  $E_n = \frac{n^2 \pi^2}{(2a)^2}$  or  $\phi_n = \sin(\frac{n\pi x}{a})$ , with  $E_n = \frac{n^2 \pi^2}{a^2}$ .

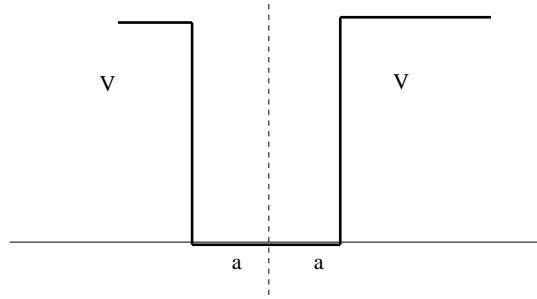


Figure 7: Figure shows an infinite square well.

## 5 Harmonic Oscillator

Consider Harmonic Oscillator with Hamiltonian

$$H = \frac{p^2}{2m} + \frac{1}{2}kx^2. \quad (39)$$

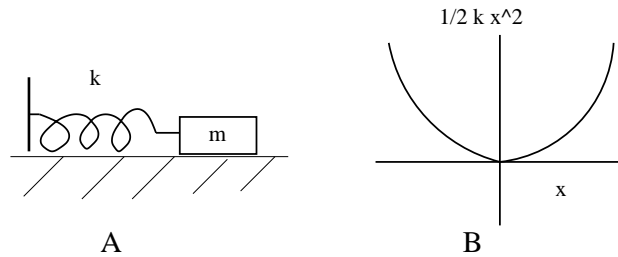


Figure 8: Figure A shows a spring-mass system, a harmonic oscillator. Fig. B shows the quadratic potential

Let  $\omega_0^2 = \frac{k}{m}$ , be the natural frequency of the oscillator. Then the Hamiltonian takes the form

$$H = \frac{p^2}{2m} + \frac{1}{2}m\omega_0^2 x^2 = \frac{1}{2}\hbar\omega_0 \left( \frac{p^2}{m\hbar\omega_0} + \frac{1}{\hbar}m\omega_0 x^2 \right). \quad (40)$$

We can further write it as

$$H = \hbar\omega_0 \left( a^\dagger a + \frac{1}{2} \right), \quad (41)$$

where

$$a = \sqrt{\frac{m\omega_0}{2\hbar}}x + i\frac{p}{\sqrt{2m\hbar\omega_0}} = X + iP \quad (42)$$

$$a^\dagger = \sqrt{\frac{m\omega_0}{2\hbar}}x - i\frac{p}{\sqrt{2m\hbar\omega_0}} = X - iP, \quad (43)$$

where as before  $p = \frac{\hbar}{i}\frac{\partial}{\partial x}$  and we use the commutation relation  $[\frac{\partial}{\partial x}, x] = 1$  or  $[p, x] = -i\hbar$ . Then we get

$$[aa^\dagger] = \hbar\omega_0. \quad (44)$$

Now as before we want to find eigenfunctions of  $H$ . The reason for writing  $H$  in terms of operator  $a, a^\dagger$  is that it helps to find these eigenfunctions. Lets see how. If  $\phi$  is an eigenvector with eigenvalue  $E$ , then  $a\phi$  and  $a^\dagger\phi$  are both eigenfunctions with eigenvalues  $E - \hbar\omega_0$  and  $E + \hbar\omega_0$  respectively.

To see this

$$\hbar\omega_0(a^\dagger a + \frac{1}{2})a\phi = a\hbar\omega_0(a^\dagger a - \frac{1}{2})\phi = (E - \hbar\omega_0)a\phi. \quad (45)$$

$$\hbar\omega_0(a^\dagger a + \frac{1}{2})a^\dagger\phi = a^\dagger\hbar\omega_0(a^\dagger a + \frac{3}{2})\phi = (E + \hbar\omega_0)a^\dagger\phi. \quad (46)$$

Therefore  $a$  and  $a^\dagger$  are called lowering and raising or annihilation and creation operators respectively. Observe energy has to be positive so we cannot keep lowering the energy. It means there is a  $\phi_0$  such that

$$a\phi_0 = 0, \quad (47)$$

which gives

$$\frac{\partial\phi_0}{\partial x} = -\frac{m\omega_0}{2\hbar}x\phi_0. \quad (48)$$

This can be integrated to get a unique solution

$$\phi_0(x) = C \exp(-\frac{x^2 m\omega_0}{4\hbar}), \quad (49)$$

with energy  $\frac{\hbar\omega_0}{2}$ . All other eigenfunctions can be derived by raising  $\phi_0$  as

$$\phi_1 = a^\dagger\phi_0 = D x \exp(-\frac{x^2 m\omega_0}{4\hbar}), \quad (50)$$

with energy  $\frac{3\hbar\omega_0}{2}$ . These eigenfunctions are called Hermite polynomials

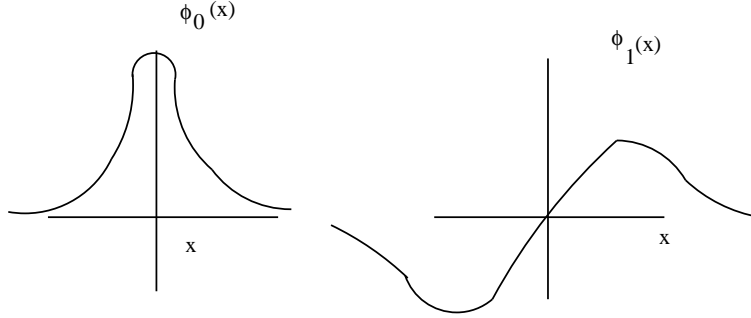


Figure 9: Figure shows first two Hermite polynomials.

## 6 Hydrogen Atom

In polar coordinates  $r = \sqrt{x^2 + y^2}$  and  $\phi = \tan^{-1}(\frac{y}{x})$ .

Then

$$\begin{aligned}\frac{\partial}{\partial x} &= \frac{\partial r}{\partial x} \frac{\partial}{\partial r} + \frac{\partial \phi}{\partial x} \frac{\partial}{\partial \phi} = \cos \phi \frac{\partial}{\partial r} - \frac{\sin \phi}{r} \frac{\partial}{\partial \phi} \\ \frac{\partial}{\partial y} &= \frac{\partial r}{\partial y} \frac{\partial}{\partial r} + \frac{\partial \phi}{\partial y} \frac{\partial}{\partial \phi} = \sin \phi \frac{\partial}{\partial r} + \frac{\cos \phi}{r} \frac{\partial}{\partial \phi}.\end{aligned}$$

$$\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial \phi^2}.$$

$$\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} = \frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial r^2} + \frac{1}{r} \frac{\partial}{\partial r} + \frac{1}{r^2} \frac{\partial}{\partial \phi^2}.$$

Using  $R = \sqrt{z^2 + r^2}$  and  $\theta = \tan^{-1}(\frac{r}{z})$ .

$$\begin{aligned}\frac{\partial^2}{\partial z^2} + \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} &= \frac{\partial^2}{\partial R^2} + \frac{2}{R} \frac{\partial}{\partial R} + \frac{1}{R^2} \frac{\partial}{\partial \theta^2} + \frac{\cot \theta}{R^2} \frac{\partial}{\partial \theta} + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \\ &= \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2}.\end{aligned}$$

To Schroedinger Eigenvalue Eq. reads

$$\left\{ \frac{\hbar^2}{2m} \left( \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \right) + (E - V(R)) \right\} \psi = 0.$$

$$\left\{ \left( \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} \right) + \frac{2mR^2}{\hbar^2} (E - V(R)) \right\} \psi = 0.$$

We write the solution  $\psi = f(R)Y(\theta, \phi)$ .

$$\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{\sin^2 \theta} \frac{\partial}{\partial \phi^2} + \underbrace{l(l+1)}_{E_1} \right) Y(\theta, \phi) = 0. \quad (51)$$

Writing  $Y(\theta, \phi) = \Theta(\theta)e^{im\phi}$ , we get

$$\left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) - \frac{1}{\sin^2 \theta} m^2 + \underbrace{l(l+1)}_{E_1} \right) \Theta(\theta) = 0.$$

For  $x = \cos \theta$ , the above equation reads

$$(1-x^2)\Theta'' - 2x\Theta' + (l(l+1) - \frac{m^2}{1-x^2})\Theta = 0.$$

The solution  $\Theta_l^m$  exists for integer  $l, m$  satisfying  $0 \leq |m| \leq l$ . For  $m \geq 0$

$$\Theta_l^m(x) = \frac{(-1)^m}{2^l l!} (1-x^2)^{\frac{m}{2}} \frac{d^{l+m}}{dx^{l+m}} (x^2-1)^l.$$

with

$$\Theta_l^{-m}(x) = (-1)^m \frac{(l-m)!}{(l+m)!} \Theta_l^m(x).$$

Then the equation for  $R$  gives

$$\frac{\partial}{\partial R} (R^2 \frac{\partial f}{\partial R}) = (l(l+1) + \frac{2mR^2}{\hbar^2} (V(R) - E)) f.$$

Let  $u = Rf$ , then

$$-\frac{\hbar^2}{2m} \frac{\partial^2 u}{\partial R^2} + (V + \frac{\hbar^2}{2mR^2} l(l+1)) u = Eu,$$

where  $V = \frac{-e^2}{4\pi\epsilon_0 r}$ . This is one-dimensional Schroedinger equation. Guess a solution of the form  $u(r) = R^{l+1} e^{-\frac{R}{a_0}}$ . Then twice differentiating  $R^{l+1}$  cancels the centrifugal part. Differentiating  $R^{l+1}$  and  $e^{-\frac{R}{a_0}}$ , cancels  $V$ , when  $\frac{\hbar^2 l+1}{m a_0} = \frac{e^2}{4\pi\epsilon_0}$ , i.e,

$$a_0 = \frac{(l+1)\hbar^2 4\pi\epsilon_0}{me^2}, \quad E = \frac{\hbar^2}{2ma_0^2}.$$

However, we don't have to cancel  $V$  immediately. We can add another term

$$u(r) = R^{l+1}e^{-\frac{R}{a_0}} + c_1 R^{l+2}e^{-\frac{R}{a_0}}.$$

Then centrifugal part of second term  $c_1$  can cancel the part of first term obtained by differentiating  $R^{l+1}$  and  $e^{-\frac{R}{a_0}}$ . For this  $c_1$  has to be chosen correct. Now we cancel  $V$  by differentiating  $R^{l+2}$  and  $e^{-\frac{R}{a_0}}$ .

Then in general

$$u(r) = R^{l+1}e^{-\frac{R}{a_0}}(1 + \sum_{j=1}^d c_j R^j),$$

with  $n = l + d + 1$ , the principle quantum number. Then

$$\frac{\hbar^2 n}{m a_0} = \frac{e^2}{4\pi\epsilon_0}. \quad a_0 \propto n$$

and

$$\frac{c_j}{c_{j-1}} = \frac{2(l+j-n)a_0^{-1}}{j(2l+j+1)}.$$

This gives  $a_0$  and finally

$$E = \frac{\hbar^2}{2ma_0^2}, \quad E \propto \frac{1}{n^2}.$$

## 6.1 Angular Momentum

$$L = r \times p.$$

$$L_x = yp_z - zp_y, \quad L_y = zp_x - xp_z, \quad L_z = xp_y - yp_x.$$

Using  $[p_x, x] = -i\hbar$ , etc, we have

$$L^2 = L_x^2 + L_y^2 + L_z^2 = R^2(p_x^2 + p_y^2 + p_z^2) - (xp_x + yp_y + zp_z - i\hbar)^2 + \hbar^2.$$

A quick calculation shows

$$xp_x + yp_y + zp_z = -i\hbar R \frac{\partial}{\partial R}.$$

Now substituting for

$$p_x^2 + p_y^2 + p_z^2 = -\hbar^2 \left( \frac{1}{R^2} \frac{\partial}{\partial R} (R^2 \frac{\partial}{\partial R}) + \frac{1}{R^2 \sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \right) \quad (52)$$

$$L^2 = -\hbar^2 \left( \frac{1}{\sin \theta} \frac{\partial}{\partial \theta} (\sin \theta \frac{\partial}{\partial \theta}) + \frac{1}{R^2 \sin^2 \theta} \frac{\partial}{\partial \phi^2} \right). \quad (53)$$

Then from Eq. 51,

$$L^2 Y(\theta, \phi) = \hbar^2 l(l+1).$$

and

$$L_z Y(\theta, \phi) = -i\hbar \frac{\partial}{\partial \phi} Y(\theta, \phi) = \hbar m Y(\theta, \phi).$$

We denote the eigenfunction as  $Y_{lm}$

Observe easily verifiable commutation relations

$$[L_x, L_y] = i\hbar L_z, \quad [L_y, L_z] = i\hbar L_x, \quad [L_z, L_x] = i\hbar L_y. \quad (54)$$

Define  $L^- = L_x - iL_y$  and  $L^+ = L_x + iL_y$ .  $L^-$  is called lowering operator and  $L^+$  is called raising operator.

$$[L^2, L^\pm] = 0, \quad [L_z, L^\pm] = \pm \hbar L^\pm. \quad (55)$$

Then note  $[L^2, L^\pm] Y_{lm} = 0$  implies  $L^2 L^\pm Y_{lm} = \hbar^2 l(l+1) L^\pm Y_{lm}$  hence  $L^\pm Y_{lm}$  is a linear combination of  $Y_{lm}$  for different  $m$ . Now  $[L_z, L^+] Y_{lm} = L^+ Y_{lm}$  implying  $L_z L^+ Y_{lm} = \hbar(m+1) L^+ Y_{lm}$  implying  $L^+ Y_{lm} = a_m Y_{l, m+1}$ . Similarly  $L^- Y_{lm} = b_m Y_{l, m-1}$ . Then observe  $L^+ Y_{ll} = 0$  and  $L^- Y_{l, -l} = 0$ . Furthermore

$$[L^+, L^-] = 2\hbar L_z. \quad (56)$$

Furthermore we get

$$L^+ L^- + L^- L^+ = 2(L^2 - L_z^2). \quad (57)$$

Then we get

$$L^+ L^- = L^2 - L_z^2 + \hbar L_z \quad (58)$$

$$L^- L^+ = L^2 - L_z^2 - \hbar L_z. \quad (59)$$

For normalized  $Y_{lm}$  we get



$$b_{lm} = \hbar\sqrt{l(l+1) - m(m-1)} \quad (60)$$

$$a_{lm} = \hbar\sqrt{l(l+1) - m(m+1)} \quad (61)$$

We talked about orbitals with principle quantum number  $n$  and integer angular momentum number  $l$  and  $z$  angular momentum  $l$ , with  $|m| \leq l \leq n - 1$ . Here  $l$  was integer. In principle it can be half integer and is ascribed to an intrinsic angular momentum called spin. We use the quantum number  $s$  instead of  $l$ . In particular  $s = \frac{1}{2}$  is called spin  $\frac{1}{2}$  a property of electron. We then have two values of  $s_z = \pm\frac{1}{2}$ . Then an electron has two sets of quantum numbers  $l, m$  and  $s, s_z$ .

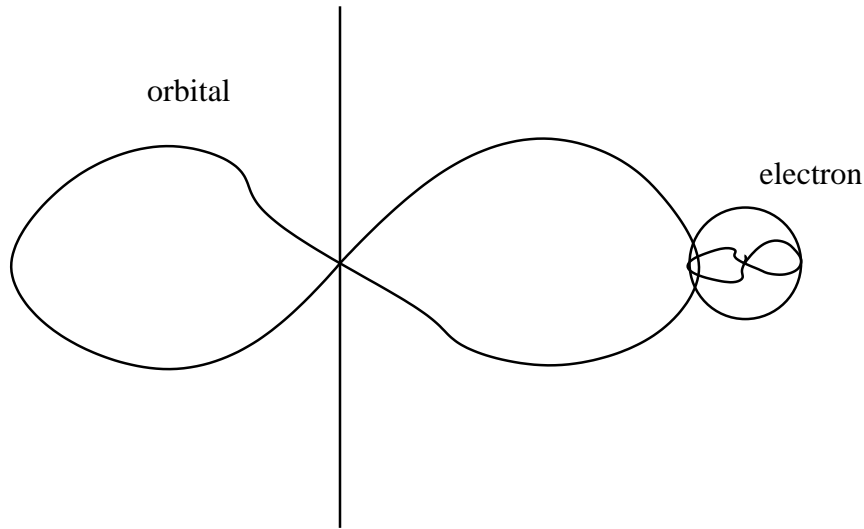


Figure 10: Fig. shows an atomic orbital and an electron with an inner orbital that constitutes its spin angular momentum

## 7 Perturbation Theory

In quantum mechanics, we are faced with a situation that we have a Hamiltonian and we calculate its eigenvalues and eigenvectors (energies and orbitals) and then we perturb the Hamiltonian slightly, this could be say application of electric or magnetic fields. We want to know how the eigenvalues and eigenvectors change when the perturbation is small.

To make matters more concrete suppose I have a matrix  $H_0$  whose eigenvalues and eigenvectors I have calculated and I change  $H_0 \rightarrow H_0 + \lambda H_1$  where  $\lambda$  is a small perturbation. We want to know how the eigenvalues and eigenvectors change. To fix ideas consider

$$H_0 = \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix}$$

its eigenvectors are  $\begin{bmatrix} 1 \\ 0 \end{bmatrix}$  and  $\begin{bmatrix} 0 \\ 1 \end{bmatrix}$  with eigenvalues 1 and  $-1$  respectively and I perturb

$$H_0 \rightarrow \begin{bmatrix} 1 & 0 \\ 0 & -1 \end{bmatrix} + \lambda \begin{bmatrix} 0 & 1 \\ 1 & 0 \end{bmatrix}$$

We can calculate the eigenvalues and eigenvectors they are  $\sqrt{1 + \lambda^2}$  and  $-\sqrt{1 + \lambda^2}$  with eigenvectors  $\begin{bmatrix} \cos \lambda' \\ \sin \lambda' \end{bmatrix}$  and  $\begin{bmatrix} -\sin \lambda' \\ \cos \lambda' \end{bmatrix}$  respectively where  $\lambda' = \frac{\lambda}{1 + \lambda^2}$ . We can expand the new eigenvalues and eigenvectors in terms of  $\lambda$  as

$$\sqrt{1 + \lambda^2} = 1 + \frac{\lambda^2}{2} - \frac{\lambda^4}{8} + \dots$$

similarly we can expand

$$\begin{bmatrix} \cos \lambda' \\ \sin \lambda' \end{bmatrix} = \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \lambda \begin{bmatrix} 0 \\ 1 \end{bmatrix} - \frac{\lambda^2}{2} \begin{bmatrix} 1 \\ 0 \end{bmatrix} + \dots$$

what do we find, the new eigenvalues and eigenvectors can be expanded as a power series in perturbation parameter  $\lambda$ .

Let  $e_i$  be eigenvector of  $H_0$  with eigenvalue  $E_i$ , after I perturb we can write the new eigenvalues as a power series

$$E_i \rightarrow E_i + \lambda E_i' + \lambda^2 E_i'' + \dots \quad (62)$$

$$e_i \rightarrow e_i + \lambda e_i' + \lambda^2 e_i'' + \dots \quad (63)$$

lets compute these corrections. We are saying

$$(H_0 + \lambda H_1)(e_i + \lambda e_i' + \lambda^2 e_i'' + \dots) = (E_i + \lambda E_i' + \lambda^2 E_i'' + \dots)(e_i + \lambda e_i' + \lambda^2 e_i'' + \dots) \quad (64)$$

Now just match terms in powers of  $\lambda$ . We get

$$H_0 e_i = E_i e_i \quad (65)$$

$$H_0 e_i' + H_1 e_i = E_i e_i' + E_i' e_i \quad (66)$$

First note  $e_i + \lambda e_i' + \lambda^2 e_i'' + \dots$  is a unit vector then this implies that  $e_i'^{\dagger} e_i$  is imaginary which gives that

$$E'_i = e_i^\dagger H_1 e_i \quad (67)$$

We can expand  $e'_i = \sum_j \alpha_{ij} e_j$ , where  $\alpha_{ij}$  is imaginary as just argued. Then E. (66) gives,

$$H_0 \sum_j \alpha_{ij} e_j + H_1 e_i = E_i \alpha_{ij} e_j + E'_i e_i \sum_j \alpha_{ij} (E_j - E_i) e_j = (E'_i - H_1) e_i. \quad (68)$$

This gives for  $i \neq j$  we have  $\alpha_{ij} = \frac{e_j^\dagger H_1 e_i}{E_i - E_j}$ . where we assume  $E_i$  are non-degenerate. Now

$$H_0 e''_i + H_1 e'_i = E_i e''_i + E''_i e_i + E'_i e'_i. \quad (69)$$

This gives

$$E''_i = e_i^\dagger H_1 e'_i = \sum_{i \neq j} \frac{e_i^\dagger H_1 e_j e_j^\dagger H_1 e_i}{E_i - E_j} \quad (70)$$

Eq. (67 and 70) give the first and second order change of energies. These are important enough to memorize.